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Dissolution Treatment of Depleted Uranium Waste

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Contents

Researchers at LLNL have developed a 3-stage process that converts pyrophoric depleted uranium metal turnings to a solidified final product that can be transported to and buried at a permitted land disposal site. The three process stages are: 1) pretreatment 2) dissolution and 3) solidification. Each stage was developed following extensive experimentation. This report presents the results of our experimental studies.

BACKGROUND

Uranium is a silvery metallic element that is found in the earth's crust in trace quantities. Uranium metal is highly reactive because its valence electrons (structure = $[Rn]5f^3 6d^1 7s^2$) are very easily oxidized. In fact, finely divided uranium powders may burn spontaneously. In nature, several isotopes of uranium are found. The abundance of the naturally occurring uranium isotopes ^{234}U, ^{235}U, ^{238}U is 0.005, 0.72 and 99.275% respectively. When the abundance of ^{235}U in a specimen is less than 0.7% it is considered "depleted". Depleted uranium is a byproduct of the enrichment process used to generate fissionable materials for weapons and energy production. What is referred to as depleted uranium metal may be pure elemental uranium or an alloy of uranium with other metals such as niobium, molybdenum, iron, or titanium.

Lawrence Livermore National Laboratory (LLNL) has an inventory of at least 11,700 kg (33 m^3) of pyrophoric depleted-uranium metal waste that requires treatment to render it suitable for disposal. Waste depleted uranium metal can be found in many physical forms including chips, turnings, chunks, sludges, and large fragments. Typically pyrophoric uranium wastes are placed in steel drums and covered with liquid (either coolant, mineral oil, or water) prior to storage. Depleted uranium waste is problematic for several reasons including its toxicity, radioactivity, and pyrophoricity.

Of depleted uranium's three hazardous characteristics, its pyrophoricity is the one that provides the greatest impediment to disposal. Because of the considerable hazards associated with depleted uranium, the storage, treatment, and disposal of uranium wastes are strictly regulated by the Environmental Protection Agency to ensure that human health and environmental integrity are protected. In addition, the U.S. Department of Transportation strictly controls the transport of pyrophoric materials. The Nevada Test Site (NTS) has stringent waste acceptance criteria but appears to be the most viable disposal location for LLNL's depleted uranium waste. The NTS Waste Acceptance Criteria (WAC) document specifies requirements that must be met, before a waste is considered suitable for disposal at their permitted land disposal site. NTS requires that fine particles in waste packages be limited to no more than 1 wt% for particles less than 10^{-6} m diameter and 15 wt% for particles less than 200 m^{-6} diameter. Three types of waste packages are acceptable for NTS disposal 1) 55 gal drum, 2) 4x4x7 box, or 3) 4x2x7 box. The maximum weight of waste per container is limited to 9000 and 1200 lbs for boxes and drums respectively. Most importantly for DU disposal, the NTS WAC requirement 3.1.11 states that waste accepted at NTS must not be pyrophoric and that any pyrophoric materials in the waste shall be treated, prepared, and packaged to be non-flammable. NTS has also established an action level of 1.5 Ci/m^3 for depleted uranium waste and carefully monitors waste which exceed this level (Hightower and Trabalka, 2000). In order to comply with disposal site waste acceptance criteria, waste management personnel at LLNL must treat depleted uranium waste onsite prior to offsite land disposal at a permitted facility.

Review of Uranium Waste Treatment Processes

There are no viable, commercially available non-thermal treatment options for mixed waste pyrophoric uranium wastes and the options available for low level pyrophoric uranium wastes are very expensive. Currently, at Oak Ridge National Laboratory, uranium chips are oxidized in a thermal treatment unit at high temperatures. Los Alamos National Laboratory (LANL) has developed a sodium hypochlorite (NaOCl) dissolution process for DU treatment, but never deployed the process at full-scale due to technical difficulties (Lussiez and Zygmunt, 1993). At LANL, they are currently stabilizing low level only (not mixed) DU and land disposing of the solidified DU on-site. Czupryna et al. (1987) evaluated several of the reagent systems previously listed for the dissolution of a 0.75% titanium/depleted uranium alloy that was contaminating stainless steel armor targets. Many of the reagent systems that they expected to work were ineffective for reasons that they could not explain. Czupryna et al. concluded that 4M HCl/7 M H_3PO_4 was the most effective and practical reagent for the treatment of 0.75%Ti/U alloys.

Review of Uranium Dissolution

The dissolution of small quantities of uranium metal and alloys as an initial step for analytical procedures has become a common practice and the dissolution of large quantities of uranium is commonly used in metallic reactor fuel reprocessing. Because analytical procedures use small amounts of metal, less attention is paid to the corrosiveness and other associated hazards of the reagents being used than would be required for a full scale treatment process. In addition, parameters vital to scaling up dissolution processes for waste treatment purposes, such as rate of reaction, heat of reaction, off-gas generation, and disposal characteristics of residuals formed are often not considered when developing analytical dissolution processes. Processes used primarily for the dissolution of fuel assemblies will not be discussed in any detail, since these processes tend to be very aggressive and require highly specialized, costly capital equipment.

Uranium is a very reactive element and its metallurgical treatment and composition have pronounced effects on its corrosion and dissolution behavior. The dissolution behavior of metallic uranium is comparable to that of magnesium. It reacts vigorously with oxidizing acids, such as hydrochloric, nitric, or perchloric acid. Other mineral acids, such as sulfuric and phosphoric acids, attack uranium metal slowly. By adding a catalyst that initiates the oxidation process, the dissolution can be significantly accelerated. Another way to accelerate uranium metal dissolution is to add a complexant that is compatible with the solvent being used. The ligands displace solvent molecules that coordinate the metal ion, forming and subsequently removing the uranium complex from the metal surface. Each time a uranium ion is removed from the surface new metal surface is exposed to the action of the solvent. The stability of the complexes formed has to be significantly higher than the stability of the solvated metal ion at the surface in order to drive this process.

Most literature reporting the dissolution of uranium and uranium alloys describe dissolution methods that were developed for use as sample pretreatment and purification methods to be used in association with uranium analysis (Larsen, 1959; Katz and Rabinowitch, 1951; Rodden, 1950). While these earlier reviews provide a valuable foundation, their primary intention was to review dissolution methods as a solution-preparing step for analytical procedures to determine uranium in a matrix or to determine other constituents of interest in the uranium metal or alloy. Table 1 summarizes the reagents most frequently used in analytical procedures to dissolve uranium metal. The most effective uranium metal dissolution systems reported by these authors were either of oxidizing-acidic, oxidizing-basic, or catalyzed acidic reactions.

Table 1: Overview of uranium metal and alloy dissolution systems

Metal	**HNO_3**	**Aqua Regia**	**HNO3 HF**	**HCl +Ox**	**HCl EtOAc**	**Br2 EtOAc**	**NaOH H2O2**	**H2SO 4Ox**	**H3PO4 (hot)**
U	s	s	s	s	s	s	s	s	s
U-Zr	N	N	s	N	N	s	N	N	-*
U-Nb	N	N	s	N	N	s	s	N	-
U-Fe	s	s	s	s	s	s	N	s	s
U-Cr	N	N	N	s	s	s	N	-	-
U-Ru	N	s	N	N	N	N	N	-	-
U-Mo	N	s	N	s	N	s	s	-	-
U-Si	s	-	s	-	-	-	-	-	-
U-Pu	s	s	N	s	s	s	N	-	-
U-Ti	-	s	-	s	s	-	N	N	-

* No information s: soluble N: not soluble - no data

The most common reagent for dissolving uranium and uranium alloys is nitric acid (HNO_3). Ten molar HNO_3 is able to rapidly and completely dissolve uranium and uranium alloys at 100°C. Violent explosion can occur during the HNO_3 dissolution of uranium alloys containing zirconium and/or niobium due to the accumulation of explosive metallic residues.

Hydrofluoric acid (HF) addition can prevent explosive reactions during HNO_3 dissolution. Strong (70%) perchloric acid $HClO_4$ at high temperatures (as high as 90°C) rapidly dissolves uranium as does aqua regia. These reagent systems will not be evaluated for onsite depleted uranium treatment because of the extremely aggressive nature of these reagents and the multiple hazards associated with their use. Hydrochloric acid (HCl) also dissolves uranium and uranium alloys rapidly with the extent of reaction dependent on both temperature and HCl concentration. Uranium dissolution with HCl results in the formation of a hydrated oxide and the evolution of hydrogen gas. The addition of phosphoric acid (H_3PO_4) prevents the formation of the potentially pyrophoric hydrated oxide particles and results in the formation of a uranyl halide solution. Larsen (1959) reports that a 4 M HCl/7 M H_3PO_4 solution will completely dissolve a bulk uranium sample in less than 30 minutes. No temperature was given for this reaction. Mixtures of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) with trace amounts of HCl at 75°C can dissolve uranium in less than 30 minutes. The liquid to solid ratio for this system is 100 mL of reagent for every 10 g of uranium dissolved. Two non-acidic chemical dissolution methods have been reported. The first involves the dissolution of uranium alloys using heavy metal salts of mercury (II), silver (I), or copper (II). In the second non-acidic method a 1 molar sodium hydroxide: 5 molar hydrogen peroxide solution was used to dissolve a 10 g sample of uranium in less than 1 hour at 100°C (Larsen, 1959).

Scope of Work

The objective of this project was to develop a chemical dissolution treatment process for waste DU chips, turnings, and sludges. Although uranium dissolution is discussed extensively in the literature, information that is pertinent to the use of chemical dissolution as a treatment process is lacking. Our desire was to develop and design a treatment process that could treat up to 80 kg of DU a day. At this larger scale, more attention would need to be paid to the hazards associated with the dissolution of uranium with the different reagents. It is essential that the dissolution process developed for DU treatment remain under the operator's control for the entire duration of treatment. Uranium dissolution reagents that result in rapid and significant heat generation at an analytical scale may be uncontrollable at this larger scale. The characteristics and storage conditions of depleted uranium waste vary from those of metal and alloy samples that analytical procedures are designed for. Waste depleted uranium is stored submerged in liquid such as coolant, mineral oil or water to minimize contact with air. In addition, within any given waste container a mixture of metals (uranium alloy, pure DU, other metals) and waste forms (sludge, turnings, chips, chunks) may be found. With mixed (low level and hazardous) DU waste, the hazardous constituents in the waste must be treated to meet RCRA disposal requirements in addition to processing the waste to remove the pyrophoric characteristic of the waste. The behavior and fate of hazardous constituents such as volatile organic compounds and toxic metals during and following DU treatment need to be understood and may influence the selection of the uranium dissolution reagents. In order to address these information gaps we evaluated uranium dissolution extensively. This report will focus on our screening studies with multiple reagent systems and detailed studies of sulfuric and nitric acid based dissolution systems. Laboratory evaluation of depleted uranium waste pre-treatment requirements will be briefly discussed.

We began our work with a screening study designed to evaluate many of the acid systems reported in the literature to determine which systems might be applicable to depleted uranium waste. Our studies were designed to explore as many systems as possible while minimizing the amount of low level and mixed waste generated as a result of our experimentation. Reagent systems that were screened included sulfuric, phosphoric, nitric, and hydrochloric acid, hydrogen peroxide, sodium hypochorite, and sodium hydroxide used either individually or in combination. We evaluated the dissolution systems in series, beginning with the least aggressive system. Following the initial screening experiments, nitric and sulfuric acid systems were studied at a larger scale. During these larger scale studies the kinetics and thermodynamics of the dissolution reactions were investigated.

Our desire was to develop a comprehensive waste treatment process. In support of this objective, we also evaluated pre-treatment that would be required prior to waste depleted uranium dissolution treatment. Waste depleted uranium turnings are typically stored in 30 and 55 gal drums while immersed in a storage solution in order to minimize contact with air. Many of the depleted uranium storage solutions have a high concentration of organic compounds which are incompatible with the acids selected for dissolution. For some of the mixed waste depleted uranium, the hazardous constituents are dissolved in the storage solution. Pretreatment includes separating the turnings from the storage solution and washing the turnings to remove traces of storage solution from the depleted uranium solids to obtain a defined and reproducible starting condition for the subsequent acid dissolution stage. A pretreatment study was completed to determine the most effective method to prepare the depleted uranium waste for acid dissolution treatment.

URANIUM DISSOLUTION SCREENING STUDY

The objective of the DU dissolution screening study was to identify the dissolution systems most applicable to the treatment of LLNL depleted uranium waste. The following criteria were established as being essential for a waste DU dissolution system:

- <u>Operating conditions</u>: The reagent system selected must proceed at an acceptable dissolution rate at ambient temperature and pressure. It was our desire to avoid the energy costs and potential hazards associated with heating treatment reagents, prior to DU treatment.
- <u>Treatment time:</u> The reagent system selected must be capable of completely dissolving uranium in a reasonable time period. The dissolution time must be less than 6 hours to allow a batch of waste to be dissolved during 1 work day.
- <u>Applicability:</u> The reagent system selected must meet the above 2 criteria for pure uranium metals and uranium alloys. The reagent system must also be applicable to turnings, sludges and chips.

The dissolution processes that met the essential treatment criteria listed above were then further compared using the following criteria, listed in descending order of significance, to facilitate the selection of the system most suitable for full-scale implementation:

- <u>Hazardous by-products:</u> The generation of hazardous reaction products that would compromise worker safety or require further treatment must be avoided.

- Temperature increase: All dissolution reactions evaluated were exothermic. It was our desire to select an effective dissolution system that had acceptable reaction rates with the least increase in temperature.
- Off-gas: Many of the dissolutions systems evaluated generated an off-gas during dissolution. Processes with no or minimal off-gases were preferred over those that generated a larger volume of off-gas.
- Corrosiveness: The least aggressive reagent solution that met the essential criteria was desired in order to minimize worker hazard and equipment cost. Some of the more aggressive reagent systems may require equipment constructed of costly materials.
- Complexity: The least complex dissolution system with the fewest required treatment steps was desired.
- Final waste volume: Because offsite disposal costs are based on the volume of waste, reagent systems that generated lower volumes of residuals were preferred over those that generated larger volumes.

In summary, it was our desire to select a uranium dissolution reagent system that could safely and completely dissolve depleted uranium metal and alloys at ambient conditions in an 8 hour work shift with out the generation of hazardous byproducts and with the least production of residuals requiring solidification.

Experimental Methods and Materials

Depleted uranium turnings for this study were obtained from the Manufacturing and Materials Engineering Division of LLNL. Turnings of pure depleted uranium and the uranium alloy U-2%Mo were collected in three different sizes; 4, 8 and 16 mil. Theses turnings had been stored without immersion in a storage solution and were used without any pretreatment. Dissolution solutions used were prepared with reagent grade acids and bases. Screening experiments were conducted in 65 mL glass test tubes into which the desired volume of dissolution solution and 1 g of turnings were placed. The dissolution solutions were heated to the desired temperature, prior to the addition of the depleted uranium turnings. Mixing was accomplished using a vortex mixer with a test tube adapter for several of the experiments. After the depleted uranium was added to the dissolution solution, the time required for complete dissolution was recorded. The amount, if any, of off-gas generated was observed and recorded. In some cases, the increase in temperature was also recorded.

Screening Study Results and Discussion

The systems evaluated have been grouped according to the major constituent of the dissolution system. The following systems achieved complete dissolution or reaction with the uranium and will be discussed in detail: 1) sodium hypochlorite, 2) nitric acid based systems, 3) sulfuric acid based systems, and 4) hydrochloric acid systems. Generally, the findings discussed in this section are our observations of the interaction of the media with the DU turnings. In most cases, the DU alloy containing 2% Mo behaved similarly to the pure DU. Where differences in dissolution behavior of the alloy were observed, it will be noted in this report.

Sodium Hydroxide – Hydrogen Peroxide

Mixtures of hydrogen peroxide and sodium hydroxide will dissolve uranium metal at a moderate rate. Larsen (1959) reported that 10 grams of uranium metal will dissolve in 50 mL of 5 mol/L hydrogen peroxide (H_2O_2) and 1 mol/L sodium hydroxide (NaOH) solution at 100 C in less than an hour forming a highly colored solution containing soluble uranyl peroxide complexes and sodium peruranates. Larsen noted that increasing the hydroxide concentration did not accelerate the dissolution. Dong (1996) reported the successful dissolution of uranium metal foil in alkaline hydrogen peroxide solution with a rate of 0.25g U per cm2 per hour in 1.5 mol/L NaOH – 4 mol/L H_2O_2 at 60°C. Dong investigated the dependency of the dissolution rate on the sodium hydroxide and hydrogen peroxide concentration. They found that the uranium metal foil dissolution rate reached a maximum with 1.5 mol/L sodium hydroxide, but continued increasing with increasing hydrogen peroxide concentration for the full range of concentrations they studied.

We subjected DU turnings to 1 mol/L sodium hydroxide - 5 mol/L H_2O_2 solution. Using 25 mL of this solution at ambient temperature, only a small fraction of the uranium metal dissolved in 6 hours. Using 50 mL of the NaOH/ H_2O_2 mixture at elevated temperatures of 40° and 65°C, we observed an increase in the dissolution rate with only a small amount of residue remaining after 1 hour. The dissolution rate of uranium in alkaline hydrogen peroxide, was too slow at ambient temperature to meet LLNL depleted uranium treatment criteria. The need to elevate the reaction temperature to achieve acceptable dissolution rates made the alkaline hydrogen peroxide system unsuitable for the treatment of the LLNL DU waste.

Sodium Hypochlorite

Commercial strength sodium hypochlorite (NaOCl) will dissolve uranium metal at elevated temperatures. This dissolution yields a bright-yellow precipitate, presumably uranium-(VI)-oxides or oxohydroxides. At Los Alamos National Laboratory (LANL), a system to treat the waste stream of metallic uranium from machining processes was developed and patented (Sauer and Watkin, 1992). This treatment system used commercial strength sodium hypochlorite solution (bleach). The chemical process included advantages such as low-treatment temperature, inexpensive reagents and the formation of a solid end product in a very moderate exothermic reaction. The end product was assumed to be a polymeric uranium-(VI)-oxide, which explained the total insolubility in water and other conventional solvents. The patent includes a description of two examples of the dissolution of metallic uranium in 5%(wt) NaOCl solution. In the first example, uncleaned uranium turnings (e.g., with an oxide layer) were treated with NaOCl solution, resulting in the instantaneous formation of a gray-green precipitate. The precipitate was dissolved in dilute nitric acid, after which a dark-gray, metallic precipitate remained. After filtration, the pale-green solution was evaporated, yielding a bright-yellow microcrystalline solid, presumably uranyl nitrate. In the second example, the turnings had been cleaned with nitric acid, removing the oxide layer before the turnings were treated with the NaOCl solution. Evidence of the reaction given in Equation 1 was immediately observed by the formation of a bright-yellow precipitate followed by a gradual increase in temperature from ambient to 40°C. After about two hours, 12 g uranium turnings were dissolved in 150 mL NaOCl solution. However, in addition the yellow precipitate, some black material was observed and assumed to be pyrophoric uranium dioxide. The addition of 100 mL of NaOCl solution resulted in the dissolution of the black precipitate after 48 hrs of further stirring at ambient temperatures. At this point, only the yellow precipitate was observed. The insolubility of the yellow precipitate in common solvents prevented a re-crystallization. The IR-characterization indicates inclusion of water molecules and the existence of U=O bonds in the structure of the yellow precipitate. This treatment method was initially proposed for conversion to full-scale implementation at LANL. Because no comprehensive studies of the chemical system and its reaction mechanisms were found in the open literature we elected to evaluate NaOCl treatment during our screening studies.

$$2\ U + 6\ NaOCl + 4\ H_2O \bullet 2\ [UO_2(OH)_2 * H2O] + 6\ NaCl \qquad (1)$$

Using NaOCl solutions with 5% available chlorine, uranium dissolution was evaluated at temperatures ranging from 25 to 60°C and liquid to solid (L:S) ratios between 5 and 25 mL NaOCl per gram of DU (Table 2). The dissolutions resulted in the formation of a yellow precipitate which was presumed to be uranium-(VI)-oxide. Often this yellow precipitate contained the finely divided black precipitate, uranium (III/IV) oxide (UO2), which is unacceptable for the treatment process because it is pyrophoric. At ambient temperatures, adding the oxidizing agent (hydrogen peroxide) did not increase the dissolution rate of DU in NaOCl or prevent the formation of UO_2.

Table 2: Results of the sodium hypochlorite, NaOCl, based dissolution systems studied to evaluate the dissolution uranium turnings (1 g DU per experiment)

Reagent	**volume** [mL]	**Temperature** [°C]	**Dissolution Time**	**Remarks**
NaOCl [5% Cl]	25	25 40 50 60	> 24 hrs 1 hr 1 hr 30 min	U_3O_8 / UO_2 formation
NaOCl [5% Cl]	5 10 15 20	40	> 3 hrs >1 hr 30 min > 1hr	UO_2 formation
NaOCl [5% Cl] with 5 successive 1ml 30 % H_2O_2 additions	37	25	> 1 hr	vigorous off-gas generation and UO_2 formation

We concluded that a treatment temperature of at least 40°C and a L:S ratio of at least 10 ml of 5% NaOCl per gram DU are required to achieve the dissolution of both, DU and 2%Mo alloy. At a reaction temperature of 40°C, the time to complete dissolution of 1 g DU metal turning was 1 hr. This reaction will not be considered a treatment option at LLNL because of the generation of the pyrophoric UO_2 precipitate and the elevated temperature required to achieve dissolution in a reasonable time.

Hydrochloric acid containing systems

Uranium metal reacts extremely rapidly and exothermically with concentrated hydrochloric acid, generating hydrogen gas, uranium-(IV)-chloride, and UO_2 (equations 2-4). The rate of dissolution is directly proportional to the acid concentration. Increasing the acid concentration results in an increased reaction rate and decreases, but does not eliminate the formation of UO_2.

$U + 3\ HCl \rightarrow UCl_3 + 3/2\ H_2$ (2)

$UCl_3 + HCl \rightarrow UCl_4 + 1/2\ H_2$ (3)

$UCl_4 + 2\ H_2O + x\ H_2O \rightarrow UO_2 \bullet x\ H_2O + 4\ HCl$ (4)

The HCl concentration also influences the final oxidation state of the dissolved uranium. The degree of oxidation that the individual reaction achieves can easily be determined by measuring the amount of hydrogen evolved. Larsen stated in his review that when uranium is dissolved in 6 mol/L HCl, the trivalent state dominates with trace amounts of tetravalent U also being formed. In concentrated HCl (16M), uranium dissolution proceeds to the tetravalent state. The formation of the UO_2 precipitate demonstrates that although hydrochloric acid is a powerful oxidizer of uranium, it is not able to oxidize uranium to the hexavalent state and the chloride ion is not an efficient complexing agent for the soluble uranium ions. To avoid the precipitation of the finely divided, extremely pyrophoric UO2, an effective complexing agent has to be added prior to the reaction or an oxidant has to be added either with or after the addition of HCl in order to dissolve any UO_2 formed. Phosphate and fluosilicate are powerful complexants of uranium(IV) and prevent the precipitation of uranium dioxide effectively when added to hydrochloric acid. Suitable oxidants that have been reported to complete the oxidation to the hexavalent state include sodium chlorate, hydrogen peroxide, bromine, ferric, dichromate, persulfate, and nitrate. Of the possible additions to HCl, ferric and phosphate appear to be the most promising for DU treatment.

Ferric-Hydrochloric Dissolution Systems

Larsen (1959) reported that adding either sulfate or an oxidizing agent such as ferric ion to hydrochloric acid would prevent the formation of the UO_2 during the dissolution of uranium in hydrochloric acid. We were unable to confirm Larsen's findings in our studies. Reacting 1gram of DU turnings with 50 mL of 3 mol/L HCl with 0.2 mol/L $FeCl_3$ at ambient temperature produced a fine black precipitate after 2 hrs which was presumed to be UO_2. The same observation was made when 1 gram of turnings were reacted with 50 mL of 3 mol/L HCl with 0.2 mol/L $Fe_2(SO_4)_3$ at ambient temperature. The addition of iron chloride or sulfate, even in excess, did not prevent the formation of pyrophoric UO_2. Because UO_2 formation could not be prevented, these systems were deemed unacceptable as potential treatments for depleted uranium waste and were excluded from further investigation. The lengthy reaction time necessary to complete the reaction, and the excessive amounts of reagents (>25 mL per 1 g) also rendered these systems unacceptable as treatment methods.

Hydrochloric and Phosphoric Acid

Pure phosphoric acid is a colorless crystalline solid with a melting point of 42.3°C. This tribasic acid is very stable and exhibits no oxidizing properties below 350°C. The reduction of phosphoric acid can only be achieved at a high temperature with strong reducing agents such as carbon. Phosphate is a strong uranium complexing agent and prevents the precipitation of the pyrophoric uranium oxide. Concentrated, boiling phosphoric acid attacks uranium metal, and as water is driven off, a point is reached where an exothermic reaction occurs, yielding a clear uranium-(IV)-phosphate solution. If oxidizing agents are added, a uranyl phosphate solution can be obtained. Prolonged heating, however, can result in polymerization of the solution and the formation of a glassy material that is extremely resistant to chemicals. Czupryna et al. reported that adding phosphoric acid to hydrochloric acid solutions resulted in a total dissolution of the U-Ti alloy. A 16 g piece of the U-Ti alloy dissolved in 4 mol/L HCl / 7 mol/L H_3PO_4 acid mixture at 85°C in 1 hr. Larsen reported that a 5 gram sample of bulk uranium metal can be completely dissolved in 30 minutes in 4M HCl / 7M H_3PO_4 (temperature not specified).

The conditions for our initial experiments with HCl and H_3PO_4 were selected based on the findings of Czupryna et al. DU and 2%Mo-U alloy turnings were treated with 25 mL of a 7 M H_3PO_4 / 4 M HCl solution at 85°C. Both sets of 1 g metal turnings were completely dissolved in less than 1 minute. The reaction was accompanied by the vigorous generation of a colorless gas. During our follow-on studies to further evaluate the HCl/H3PO4 system for the dissolution of uranium turnings, the following parameters were varied: acid concentration, liquid to solid ratio, and temperature. Initially our primary goal was to decrease the reaction rate to the extent that treatment at a larger scale could be safely controlled. Neither decreasing the temperature nor decreasing the liquid to solid ratio affected the dissolution rate with 7 M H_3PO_4 / 4 M HCl solution. Even when using only 5 mL of the 7 M H_3PO_4 - 4 M HCl solution at ambient temperature, 1 g of DU turnings were dissolved in less than 5 minutes. Subsequently, the acid concentrations in the mixture were incrementally lowered to determine the optimum conditions for the uranium dissolution (see Table 3).

Table 3: Results of the Phosphoric – hydrochloric acid dissolution systems (H3PO4-HCl) investigated to evaluate the dissolution of uranium turnings (1 g DU turnings per experiment)

H_3PO_4 *[mol/L]*	HCl [mol/L]	**Volume** [mL]	**Temperature** [°C]	**Dissolution Time**	Remarks
7	4	5, 10, 15, 20, 25	25, 35, 45, 55, 85	< 5 min	independent of temperature or volume
7	3 2 1.5 1	10	25	6 min 10 min 30 min ~ 24 hrs	sludge-like solid forms after 2 days
6	4	10	25	4 min	
4	4 2 1	10	25	8 min 1.5 hrs 1.5 hrs	sludge-like solid forms
2	4 2 1	10	25	~ 20 min 1.5 hrs 1.5 hrs	sludge-like solid forms
1	4	10	25	~25 min	sludge-like solid forms

We observed that the reaction of the HCl/ H_3PO_4 acid mixture with the uranium metal changed from complete dissolution to complete conversion as the acid concentrations were decreased. The conversion results in the direct formation of the hygroscopic sludge-like solid. No metallic residues were observed. The change from complete dissolution to complete metal conversion occurs if the phosphoric acid concentration was equal to or below 4 mol/L or if the hydrochloric acid concentration was below 2 mol/L (Table 3). At a solid to liquid ratio of 1g metal in 10 mL of reagent mixture, very small amounts of free liquid (less than 0.1%) remain after the solid forms and only moderate gas evolution is observed. Increasing the reagent volume did not affect the dissolution rate but increased the amount of free liquid remaining, although not proportionally. The excess liquid can easily be separated from the solid by mechanical means, such as pressing, centrifugation, or drying if desired. Uranium analysis by gross alpha-beta counting determined that the excess free liquid did not contain any uranium. The uranium concentration in the liquids was below the methods minimum detectable limits of 0.6 mg/L (20 pCi/L) assuming U-238 is the sole alpha-emitter. The solids formed are greenish-gray in color, indicating the formation of a solid containing uranium in its tetravalent oxidation state. Examining the solids under a scanning electron microscope revealed a fibrous structure (Figure 1), which explains the solid's extreme hygroscopic nature, e.g., their ability to absorb large quantities of free liquids.

We hypothesize that the hydrochloric acid in the reagent mixture accomplishes the oxidation of the uranium metal in the dissolution process as shown in equation 3. The phosphoric acid, however, is a strong uranium ion complexing agent. The uranium-IV-ions formed are immediately complexed by the phosphate ions, making the conversion from metal into the phosphate solid instantaneous. This immediate complexation prevents the formation of the finely divided black UO_2 precipitate usually observed in solutions of pure hydrochloric acid. The conversion of the metal to the phosphate solid (eq. 5 and 6) results in an irreversible removal of the uranium and hydrogen phosphate ions from the reagent mixture, favoring this reaction just as much as the uranium dissolution due to the action of the hydrochloric acid.

$$U + 4\,H_3O^+ \xrightarrow{HCl} U^{4+} + 4\,H_2O + 2\,H_2 \qquad (5)$$

$$U^{4+} + x\,H_2PO_4^- \rightarrow [U(H_2PO_4)_x]^{(4-x)+} \qquad (6)$$

Although chloride containing reagent systems pose engineering challenges, the direct formation of a stable solid that is potentially suitable for direct disposal is extremely appealing.

The most efficient conditions for the uranium metal conversion by the hydrochloric – phosphoric acid mixture are 10 mL of a solution of 3 mol/L in hydrochloric acid and 1 mol/L in phosphoric acid per gram uranium metal at ambient temperature.

Figure 1: SEM photograph of the sludge like solid form in the reaction of phosphoric-hydrochloric acid with uranium metal

Nitric Acid Predominated Systems

Concentrated hot nitric acid dissolves massive uranium metal and is the most commonly used method to dissolve uranium and its alloys in analytical procedures and in nuclear fuel reprocessing. Caution has to be paid as nitric acid vapor or nitrogen dioxide can react explosively with uranium turnings, powders, or sintered materials. The dissolution reaction is complex, and the acid reduction products vary from nitrogen dioxide to ammonia. Dissolutions utilizing concentrations less than 7.5 mol/L nitric acid produce predominantly nitrous oxides (eq. 7), while at higher concentrations primarily nitrogen dioxide is generated (eq. 8). Exposing alloyed uranium to pure nitric acid has resulted in violent and sometimes explosive reactions. Fluoride or oxalate is traditionally added to prevent such violent reactions. The addition of other oxidants and complexants (such as hydrogen peroxide and phosphate) has also been successfully employed to minimize the potential for explosion.

$$4\ U + 18\ HNO_3 \rightarrow 4\ UO_2(NO_3)_2 + 3\ NO_2 + 7\ NO + 9\ H_2O \quad (7)$$

$$U + 6\ HNO_3 \rightarrow UO_2(NO_3)_2 + 3\ NO_2 + NO + 3\ H_2O \quad (8)$$

We evaluated nitric acid-based dissolution systems at ambient and slightly above ambient temperatures. The experiments were divided into three series, each evolving from the preceding series. We observed that when dissolution was achieved, no residuals remained and UO_2 precipitate was not formed in any of the treatment conditions studied during this set of experiments.

Our first attempts to dissolve uranium turnings in HNO_3 solutions of vary concentrations (1, 8, 11.5, and 15 mol/L) at room temperature proceeded extremely slowly. A reaction was observed in the experiments using 1 and 8 mol/L nitric acid and the change in color of the solution suggested the formation of the uranyl ion. After two hours, only minimal dissolution of the dosed uranium was observed and the experiments with 1 and 8 M HNO_3 at ambient temperature were terminated. With the higher concentration HNO_3 solutions (11.5 and 15 mol/L), a color change was noted and some uranium dissolution was observed after several hours. Instead of terminating this set of experiments, the turnings were left in the acid solution and complete dissolution was noted after 48 hours had elapsed. The apparent corrosion resistance of uranium metal and alloys against dilute nitric acid prompted us to increase the acid concentration. This did not substantially increase the rate of dissolution. Increasing both the acid concentration and the temperature accelerated the dissolution rates (see Table 4). At 40°C, the uranium turning partially dissolved in 10 mol/L nitric acid within 90 minutes. After terminating this experiment, the turning was weighed and subjected to 10 mol/L nitric acid at 65°C. The residual turnings (0.55 g) dissolved in 55 min. DU and 2%Mo alloy turnings were then subjected to 12 M HNO3 at 60°C. The alloy was dissolved in 1 min, and the DU turnings in 2.5 hrs.

In the second series of experiments, we studied how small additions of phosphoric (H_3PO4), hydrochloric (HCl), or sulfuric acid (H_2SO_4) to 12 molar nitric acid affected the dissolution rate of DU turnings at an initial reaction temperature of 40°C. In most experiments, the turnings were completely dissolved in less than 2 hours (Table 4). Varying the amounts of H_3PO_4 added to nitric acid did not have any effect on the dissolution rate of the turnings.

Table 4: Results of the nitric acid, HNO3, based systems investigated to evaluate the dissolution DU turnings (1 g per 25 mL).

Series	***Nitric Acid, [mol/L]***	**Additive [mol/L]**	**Temperature** [°C]	**Dissolution Time**
1	1, 8, 11.5, 15		25	1 and 8 M terminated at 2 hr 11.5 and 15 M dissolution in 48 hrs
	10		40 65	See text
	12		60	2.5 hrs
2	12	H_2SO_4 0.3 0.6 1.7	40	 2 hrs 1 hr 10 min
	12	H_3PO_4 0.3 0.6 1.7	40	 1.6 hr 1.6 hr 1.6 hr
	12	HCl 0.3 0.6 1.7	40	 0.5g dissolved after 3 hrs 1.5g dissolved after 3 hrs 30 min
3	8	H_2SO_4 0.1 1.1 2	25 (40, 70)	 not dissolved not dissolved not dissolved
	11.5	H_2SO_4 0.1 1.1 2	25 (55)	 not dissolved 1.5 hrs 20 min

	14	H_2SO_4 0.1 1.1 2	25 (40, 70)	 not dissolved 37 min 65 min

The system with the fastest dissolution rate was a mixture of 12 mol/L HNO_3 and 1.7 mol/L H_2SO_4, which dissolved 1 g of DU turning in 10 min.

The third series of experiments systematically studied the effects of varying the acid concentration and dissolution temperature. Increasing in nitric acid concentration from 8 mol/L to 11.5 mol/L while keeping the sulfuric acid concentration constant at 2 mol/L resulted in a significant increase in dissolution rate (1 hr at 40°C vs. 20 min at 25°C). A further increase in nitric acid concentration to 14 mol/L did not have a pronounced effect. Increasing the sulfuric acid concentration had a reverse effect on the dissolution rate at a nitric acid concentration of 14 mol/L. Making the solution 2 mol/L or 1.1 mol/L sulfuric acid decreased the dissolution time from 65 min to 37 min. An increase in temperature generally increased the rate of dissolution at all acid concentrations tested. For example, the reagent mixture 8 mol/L in HNO_3 and 2 mol/L in H_2SO_4, which did not dissolve uranium metal at ambient temperature, dissolved the 1 g DU turnings in a little more than one hour, when the dissolution was performed at 40 or 70C°.

The nitric acid system that is able to treat DU waste at ambient temperatures with a sufficient dissolution rate is a reagent solution, of 11.5 mol/L in HNO_3 and 2 mol/L in H_2SO_4. This system dissolves 1 g DU metal turnings in 20 min producing a yellowish-orange solution, indicative of the uranyl ion. Although this system meets the essential treatment criteria, it was not selected for further studies because of the acid concentration and residual volume exceeded those of other systems that also met the essential treatment criteria.

Sulfuric Acid Predominated Systems

Sulfuric acid is a weak oxidizing acid that does not readily dissolve uranium metal. Uranium metal is resistant to 6 mol/L sulfuric acid at boiling temperatures and is attacked slowly by hot concentrated H_2SO_4. This is due to both the weak oxidizing power of sulfuric acid and the pacifying action of the sulfate ion on the metal surface. Adding an oxidizing agent, such as nitric acid or hydrogen peroxide, to 6 mol/L sulfuric acid significantly increases the dissolution rate. The combination of the oxidizing power of the nitric acid and the complexing strength of the sulfate ion toward the uranium-(IV) and uranyl ions formed, forces the reaction in the direction of an irreversible dissolution of the metal. Larsen reported the dissolution of uranium with sulfuric acid, hydrogen peroxide and catalytic amounts of HCl.

In an attempt to replicate the experimental findings of Larsen, DU turnings were treated with a mixture of 7.4M H_2SO_4, 0.2M HCl and 0.1M H_2O_2 at 65°C. The turnings (DU and 2%Mo) were only partially dissolved in 4.5 hrs. A second addition of 1 mL 30% H_2O_2 completed the dissolution. At ambient temperature, the dissolution of uranium metal in the same reagent took 2.5 hrs for the 2%Mo alloy and 24 hrs for DU. By varying the reaction conditions, we found that the dissolution temperature for the H_2SO_4 - HCl - H_2O_2 system had to be at least 45°C, and that repeated additions of H_2O_2 are needed to achieve complete DU dissolution in a reasonable amount of time. Attempts to increase the dissolution rate by substituting the hydrochloric acid with catalytic amounts of iron (III) failed (see Table 5). The H_2SO_4/HCl/H_2O_2 system was not selected for further study due to the elevated temperatures and multiple reagent additions required for complete dissolution.

Preliminary results of our attempts to dissolve DU in the system H_2SO_4 / HNO_3 are summarized in Table 5. Sulfuric acid solutions of 12 and 3 mol/L combined with nitric acid in the range of 0.1 to 2 mol/L did not dissolve the uranium metal (Figure 2). However, solutions of 7.5 mol/L sulfuric acid and 1.1 mol/L or higher in nitric acid dissolved DU rapidly. Increasing the reaction temperature increased dissolution rate for these systems (Figure 3). However, since at ambient temperatures, 1 g of DU turnings dissolved in 25 mL of 7.5 M H_2SO_4/1.0 M HNO_3 in 20 min we chose to study the process further at ambient temperature only.

Table 5: Results of the sulfuric acid, H_2SO_4, based system investigate to evaluate the dissolution of metallic DU turnings (1 g)

H_2SO_4 [mol/L]	Additive [mol/L]	Temperature [°C]	volume [mL]	Dissolution Time	Remarks
7	0.1 to 1 mol/L H_2O_2 0.1 to 1 mol/L HCl	25, 35, 45, 65	10	< 2 hrs	Repeated H_2O_2 addition necessary
6	1 mol/L H_2O_2 0.2 mol/L $FeCl_3$	25	40	< 1 hr	UO_2 formation
6 3	1 mol/L H_2O_2	25, 60	10	not dissolved	
6	0.45 mol/L HNO_3	45, 50	30	< 30 min	
12	HNO_3 0.1 1.1 2	25 (40, 55, 70)	25	 not dissolved not dissolved not dissolved	
7.5	HNO_3 0.1 1.1 2	25 (40, 55, 70)	25	 not dissolved < 18 min < 22 min	Higher temperatures increase the rate
3	HNO_3 0.1 1.1 2	25 (40, 55, 70)	25	 not dissolved not dissolved not dissolved	

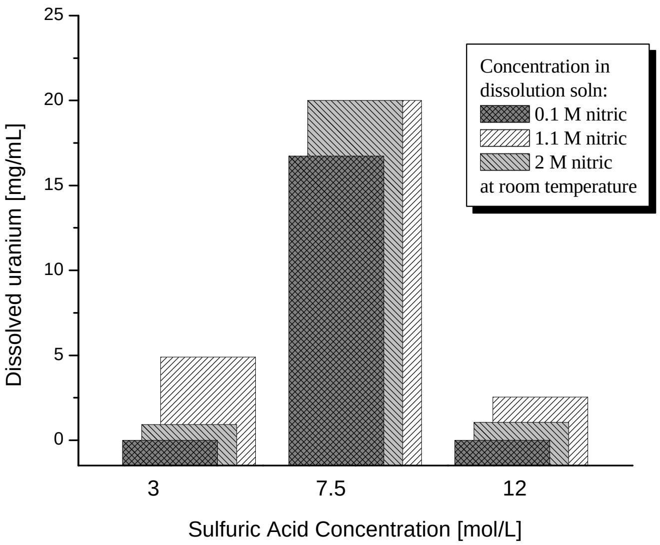

Figure 2: The amount of uranium dissolved after 2 hrs as function of sulfuric and nitric acid concentrations (initial uranium 1g, turning thickness 4 mil, temperature 25°C).

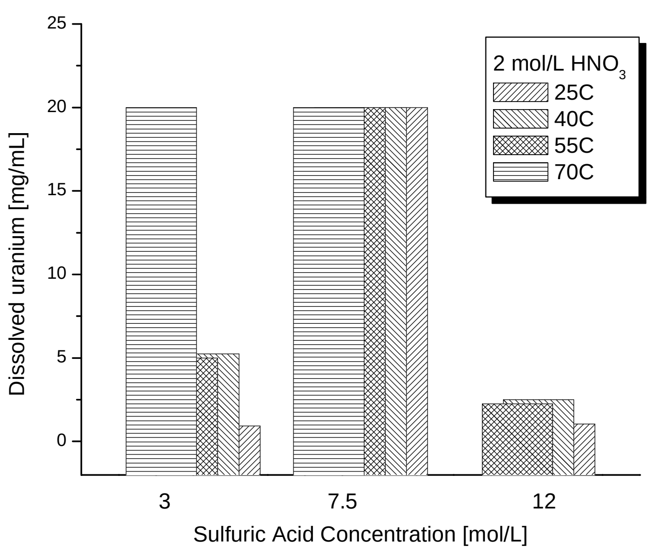

Figure 3: The amount of uranium dissolved after 2 hrs as function of temperature and sulfuric acid concentration (initial uranium 1g, turning thickness 4 mil, 2 mol/L in nitric acid)

The brown color of the gases (nitrous gases) generated during the dissolution of DU suggests the reduction of nitric acid. The color of the solution at the end of the dissolution process is the dark green color characteristic of the uranium-(IV)-ion. This suggests that once the uranium reaches its tetravalent state, the complexing characteristics of the sulfate ion prevents further oxidation (eq. 9) of the uranium-(IV)-ion to the uranyl ion. After several days, the solution turns yellowish-orange, indicating a slow oxidation of the uranium-(IV)-ion to the uranyl ion (eq 10).

$$U^{4+} + 2\ SO_4^{2-} \rightarrow U(SO_4)_2 \qquad (9)$$

$$U^{4+} + 2\ HNO_3 + 1\tfrac{1}{2}\ O_2 \rightarrow UO_2^{2+} + 2\ NO_3^{-} + H_2O \qquad (10)$$

The 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 dissolution reagent fulfilled our preliminarily selection criteria and was chosen for further investigation for the design of an LLNL onsite depleted uranium waste treatment process. The acid concentrations used are within the acceptable range for many common reactor materials. The dissolution can be performed at ambient temperature, does not produce excess amounts of heat or off-gases and proceeds at a feasible rate. After neutralization the uranyl solution can be stabilized using commercial clay or polymer based products.

SULFURIC AND NITRIC ACID DETAILED STUDIES

Following the screening study, DU dissolution with sulfuric and nitric acid was studied in more detail to determine the optimum treatment conditions for this system. An additional objective of these studies was to identify the reaction mechanism for metallic uranium dissolution in a mixture of nitric and sulfuric acid and to determine the thermodynamic and kinetic reaction parameters needed to support the scale-up of the process and the design of a full-scale deactivation treatment process for pyrophoric metallic uranium wastes.

Basic thermodynamic data have been published for uranium dissolution (Katz 1986, Wanner 1992, Cordfunke 1978, Fuger 1992). There is general agreement that U^{4+} ions exhibit a green color in solutions and UO_2^{2+} ions a yellow-orange color. The dominant UV/VIS absorption bands are observed at 630 nm and 421 nm, respectively for these ions. Katz et al. reports a uranyl ion formation enthalpy of -1019.2 ± 2.5 kJ mol-1 and formation entropy of –98 J K^{-1} mol^{-1}. Tables 6 and 7 summarize known fundamental data for uranium ions and complexes from the most recent collections of thermodynamic data by Wanner et al. and Fuger et al. that were pertinent to our investigation.

Table 6: Formation enthalpies and entropies of selected uranium ions and complexes (298.15 K)

ion (aq.)	$\Delta_F H^o_m$	S^o_m
U^{4+}	-591.2 ± 3.3	-416.9 ± 12.6
UO_2^{2+}	-1019.0 ± 1.5	-98.2 ± 3.0
USO_4^{2+}	-1492.5 ± 4.3	-245.6 ± 15.9
$U(SO_4)_2$	-2377.2 ± 4.4	-69.0 ± 16.2
UO_2SO_4	-1908.8 ± 2.2	46.0 ± 6.8
$UO_2(SO_4)_2^{2-}$	-2802.6 ± 1.9	135.8 ± 4.8
$UO_2(NO_3)_2$	-1433.4 ± 4.1	

Table 7: Complex stability constants and reaction enthalpies of selected uranium complexation reactions (298.15 K)

reaction	**complex stability constant**	**$\Delta_r H^o_m$ kJ mol^{-1}**
$U^{4+} + q\ SO_4^{2-} = U(SO_4)_q^{4-2q}$	lg β_1 = 6.6 lg β_2 = 10.5	8 ± 3 33 ± 3
$UO_2^{2+} + q\ SO_4^{2-} = UO_2(SO_4)_q^{2-2q}$	lg β_1 = 3.15 lg β_2 = 4.14	19.5 ± 1.6 35.1 ± 1.0
$UO_2^{2+} + q\ SO_4^{2-} = UO_2(SO_4)_q^{2-2q}$	lg β_1 = 3.4 lg β_2 = 4.1	4.8 ± 0.2 9.0 ± 0.5
$U^{4+} + q\ NO_3^{-} = U(NO_3)_q^{4-q}$	lg β_1 = 1.47 lg β_2 = 2.3	

Recently, Rodrigues et al. (2002) investigated the kinetics of the electrochemical dissolution of metallic uranium in nitric acid. Using the initial rate method, they determined that this dissolution is a zero-order reaction, e.g. independent of the nitric acid concentration. The proposed reaction mechanism is based on the adsorption theory, reflecting directly the observed rate law, as a zero-order reaction is often a complex reaction that is controlled by a physical process.

<u>Method and Materials</u>

Tables 8 and 9 summarize the optimization experiments which were conducted using from 5 to 50 g of depleted uranium per dissolution study. Sulfuric and nitric acid uranium dissolution experiments were conducted using a six place reaction station and 250 mL polyethylene reaction vessels. During treatment, the pH and temperature were monitored and recorded continuously until complete dissolution was observed. The dissolved uranium concentration in grab samples collected at regular intervals was monitored using a UV-VIS spectrometer. No attempt was made to monitor or measure the brown off-gas that was generated during some of this set of dissolution experiments. Later studies were conducted in which the quantity of off-gas generated was measured by capturing the off gases in a graduated cylinder inverted in a basin of water.

Determination of Optimum Uranium Metal Dissolution Conditions

Our first detailed evaluation of the sulfuric-nitric acid system was designed experiments to determine the most effective dissolution of the DU turnings at the lowest possible temperature, acid concentration, and liquid to solid ratio. An experimental plan (Tables 8 and 9) was established using the randomized half fractional factorial method incorporating the following variables of the system: H_2SO_4 concentration, HNO_3 concentration, temperature and turning thickness. The randomized half-fractional factorial experiment design included the maximum, minimum and mid point of each variable. The individual reactions were performed in a reactor station that can accommodate, stir, and heat six individual reaction vessels. Using this station we were able to run up to six reactions in parallel at the same temperature.

Depleted uranium (DU) turnings were obtained from the Manufacturing and Materials Engineering Division of LLNL. The dry-stored turnings were of known thickness: 0.1, 0.2 and 0.4 mm. The acids used were of ACS reagent grade quality. The acid mixtures were prepared by adding known amounts of the concentrated acids (sulfuric 18 mol/L, nitric 15 mol/L) to the necessary amount of double distilled water. The acid mixtures were prepared fresh each treatment day. Two grams of DU turnings were added to 50 mL of the given acid mixture at the desired temperature. The uranium was always added to the reagent mixture in the reaction vessel. Reagent solutions were heated to the desired temperature prior to adding the uranium turnings.

Two different control measures were utilized: the time to complete the dissolution or the amount of uranium dissolved in a given time period. The uranium concentrations were determined by monitoring the absorbance using an Ocean Optics UV/VIS spectrometer. The time to complete dissolution was determine visually, or if no complete dissolution was observed then the uranium concentrations was determined 2 hours after the dissolution was started.

Table 8: Experiments as generated by the randomized half fractional-factorial design method and results obtained for determining optimum uranium metal dissolution conditions of in a mixture of sulfuric and nitric acid, where nitric acid is the major component.

Temperature [°C]	**Turning Size [mm]**	**HNO_3 conc. (mol/L)**	**H_2SO_4 Conc. (mol/L)**	**Dissolved uranium after 2hrs [%]**	**Time to complete dissolution**
55	0.2	11.5	1.1	100	4 min
40	0.1	8	0.1	5	terminated
70	0.1	8	2	100	3 min
40	0.1	14	2	100	4 min
70	0.2	8	0.1	50	terminated
55	0.2	11.5	1.1	100	4 min
70	0.1	14	0.1	100	3 min
40	0.2	8	2	100	45 min
70	0.2	14	2	~50	terminated
40	0.2	14	0.1	95	4 hrs
55	0.2	11.5	1.1	100	4 min

Table 9: Experiments as generated by the randomized half fractional-factorial design method and results obtained for determining optimum uranium metal dissolution conditions of in a mixture of sulfuric and nitric acid, where sulfuric acid is the component.

Temperature [°C]	Turning Size [mm]	HNO_3 conc. (mol/L)	H_2SO_4 Conc. (mol/L)	Dissolved uranium after 2hrs [%]	Time to complete dissolution[min]
55	0.2	1.1	7.5	100	8
40	0.1	0.1	3	50	terminated
40	0.2	0.1	12	8	terminated
40	0.1	2	12	11	terminated
70	0.2	2	12	5	terminated
55	0.2	1.1	7.5	100	8
70	0.1	2	3	90	terminated
70	0.1	0.1	12	10	terminated
70	0.2	0.1	3	6	terminated
40	0.2	2	3	33	terminated
55	0.1	1.1	7.5	100	6

The randomized experiments did not yield sufficient information to determine the optimum acid concentration for uranium dissolution when sulfuric acid is the major component of the two acid system. Following the initial experiments, we performed a more systematic study of the dissolution of metallic uranium in the sulfuric and nitric acid solution. Uranium metal was subjected to all combinations of acid concentration that were utilized in our initial studies and the temperature dependency was extended to include ambient temperature. Results of these more detailed studies are illustrated in Figures 5 and 6. Figure 5 presents the amount uranium that is dissolved after two hours of reaction as a function of sulfuric acid concentration and temperature, when the nitric acid concentration is 2 mol/L in the acid solution. Figure 6 shows the amount of uranium dissolved after two hours as function of the sulfuric and nitric acid concentration at ambient temperature. In all experiments, 1-gram of 0.1 mm thick DU turning was dissolved in 50 mL of acid solution.

The system, which has sulfuric acid as the major component, was studied more comprehensively with regard to temperature, acid concentration, turning thickness, and liquid to solid ratio. A total of nine acid mixtures were evaluated for each turning thickness (0.1 and 0.2 mm) and temperature (25, 40, 55, and 70°C). One gram DU turning was dissolved in 50 mL of acid solution per experiment. These experiments are summarized in Table 10 and Figures 4 through 6. As in previous experiments, the time to complete dissolution or the uranium concentration in the solution two hours after initiating the reaction were the control measures for the reactions progress.

The effect that the turning thickness, the liquid to solid ratio, and the turning composition have on the dissolution rate of DU turning was studied for the optimum dissolution system (7.5 mol/L sulfuric – 1 mol/L nitric acid at ambient temperature). The effect of the turning thickness was evaluated by adding 1-gram of each available turning size (0.1, 0.2, and 0.4 mm) to 50 mL of the acid mixture. The time to complete dissolution of each turning sample was recorded. The effect of the solid to liquid ration of the dissolution rate was followed by adding 1-gram of the 8 mil DU turning to 15, 20, 25, and 50 mL of the acid solution and determining the time to complete dissolution. To study the effect that varying metal composition have on the dissolution rate, 1 gram of a 2wt% Molybdenum-Uranium alloy and an actual waste sample were subjected to above procedure.

Table 10: Results and experimental parameter of the sulfuric acid dominated systems that achieved complete dissolution in less than 25 minutes.

Temperature [°C]	**Turning Size [mm]**	**HNO_3 conc. (mol/L)**	**H_2SO_4 Conc. (mol/L)**	**Time to complete dissolution [min]**
25	0.1	2	7.5	15
40	0.1	2	7.5	9
55	0.1	2	7.5	4.5
70	0.1	2	7.5	< 5
25	0.1	1.1	7.5	12
40	0.1	1.1	7.5	6
55	0.1	1.1	7.5	5.5
70	0.1	1.1	7.5	<5
25	0.2	2	7.5	22
40	0.2	2	7.5	10
55	0.2	2	7.5	4.5
70	0.2	2	7.5	< 4:45
25	0.2	1.1	7.5	22
40	0.2	1.1	7.5	11
55	0.2	1.1	7.5	8
70	0.2	1.1	7.5	< 6

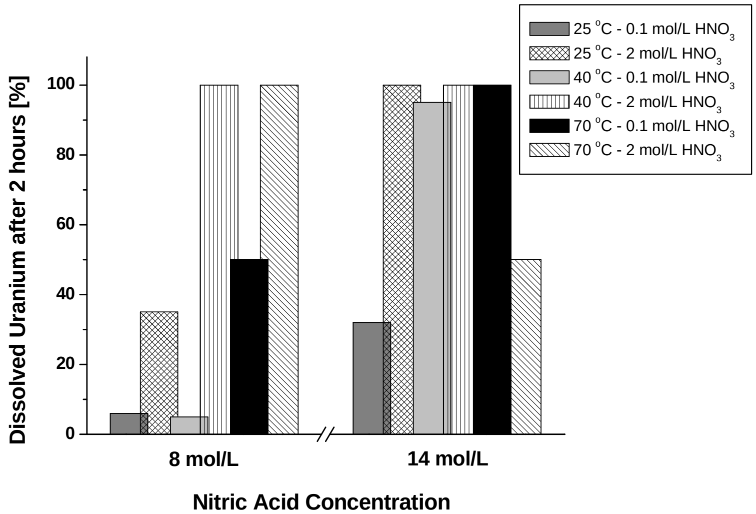

Figure 4: Amount of metallic uranium dissolved in the acid mixtures after 2 hours of reaction as function of temperature, nitric and sulfuric acid concentrations.

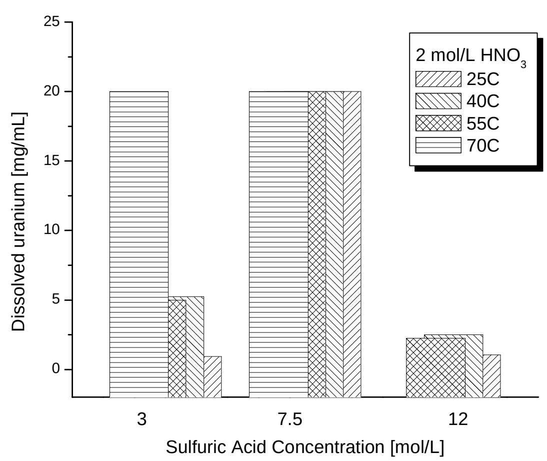

Figure 5: Amount of uranium dissolved after 2 hrs as function of H_2SO_4 concentration and temperature while holding constant the amount of DU metal (1 g), the turning thickness (0.1 mm) and the HNO_3 concentration (2mol/L).

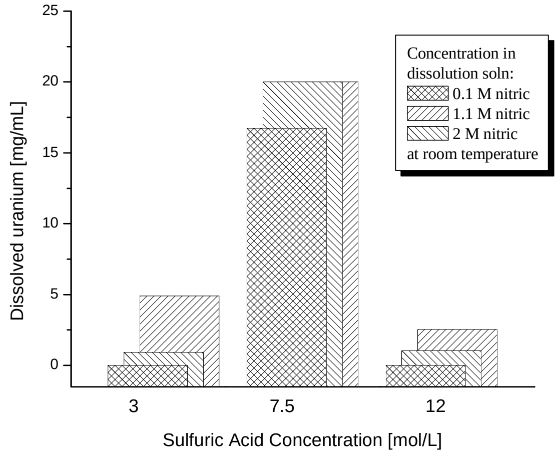

Figure 6: Amount of uranium dissolved after 2 hrs as function of H_2SO_4 and HNO_3 concentration while holding constant the amount of DU metal (1 g), the turning thickness (0.1 mm) and the temperature (25°C).

Tables 8 and 9 summarize the reaction conditions and results of the optimization studies for the dissolution of metallic uranium in a mixture of nitric and sulfuric acid. The results of metallic uranium dissolutions at the maximum and minimum acid concentrations are included in Figure 4. The results at the mid point acid concentrations are not included in Figure 4 because these studies all resulted in complete dissolution in less than 2 hours independent of the temperature the reaction was run at. We observed an increase in uranium dissolution with temperature with the exception of dissolution with 14 mol/L in nitric and 2 mol/L in sulfuric acid. The results of the optimization study have to be interpreted with caution because the randomized experimental design included several variables that may not be related and ultimately resulted in rather randomized results. However, we were able to conclude from this study that a H_2SO_4/HNO_3 acid mixture has to be at least 11.5 mol/L in nitric and 1.1. mol/L in sulfuric to achieve complete dissolution at ambient temperature in less than 2 hours.

Figure 5 demonstrates that the acid mixture 7.5 mol/L in sulfuric and 2 mol/L in nitric acid dissolves the uranium metal rapidly independent of the initial reaction temperature, while the amount of dissolved uranium metal steadily increase with increased initial reaction temperature when the acid mixture is 3 mol/L in sulfuric acid. Increasing the sulfuric acid to 12 mol/L results in decreased dissolution of uranium metal at all temperatures studied. In Figure 6 the effect that the nitric acid concentration has on the dissolution of the uranium metal is examined at room temperature. At all three evaluated sulfuric acid concentration, an increase in nitric acid resulted in an increase in amount of uranium metal dissolved in two hours. Complete dissolution of the metal in less than 2 hours was observed in acid solution 7.5 mol/L in sulfuric acid and 1.1/2 mol/L in nitric acid at ambient temperature. Table 10 summarizes all experimental conditions that resulted in the dissolution of 1-gram DU metal in less than 25 minutes.

As a follow-on to the experiments just described we conducted a series of experiments to determine if small changes in acid concentration result in significant changes in dissolution rates of the metal in the acid mixtures. The acid concentrations were varied in 0.5 mol/L steps from 7 to 8 mol/L for the sulfuric acid and from 0.5 to 1.5 mol/L for nitric acid. All reactions were performed at ambient temperature with 1-gram of 0.1 mm thick DU metal turning. The results of those optimization experiments are shown in Figures 7 and 8. The data from the previous experiments are included as reference.

As the results listed in Table 10 and Figures 7 and 8 demonstrate, the acid mixture that is 7.5 mol/L in sulfuric and 1 mol/L in nitric acid is the reagent that has the lowest acid concentration but achieves the fastest complete dissolution of the uranium metal. The 7.5 mol/L H_2SO_4 / 1 mol/L HNO_3 acid solution was the reagent that was studied in all subsequent investigations, which were designed to obtain essential information for the design of a large-scale treatment process using this mixture.

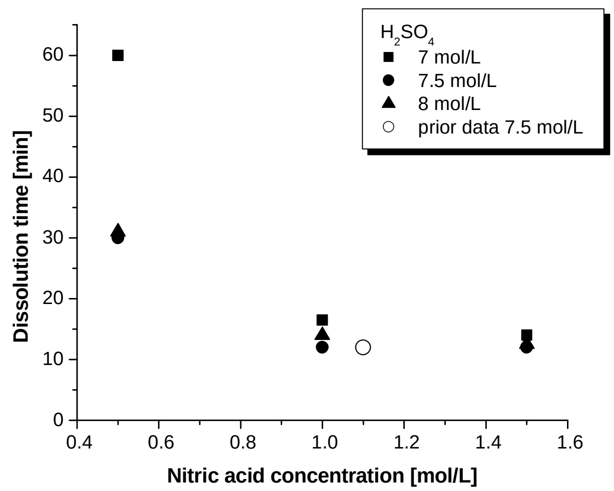

Figure 7: Time to complete dissolution of 1-gram 0.1 mm thick DU turning in 50 mL acid solution as function of nitric acid concentration.

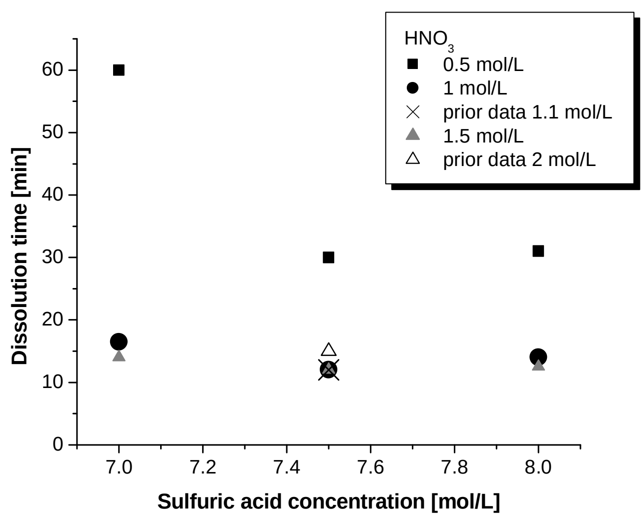

Figure 8: Time to complete dissolution of 1-gram 0.1 mm thick DU turning in 50 mL acid solution as function of sulfuric acid concentration.

After selecting 7.5 M H_2SO_4/1.0 M HNO_3 as the most suitable dissolution solution at ambient temperature, we conducted a series of experiments to determine the minimum volume of acid solution that would be required to dissolve uranium in a reasonable amount of time.

Minimizing the reagent volume acid used will minimize the amount of secondary waste generated, and will ultimately minimize the volume of stabilized waste to be disposed. The results of this study are summarized in Figure 9. We determined that a minimum volume of 20 mL of 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 acid solution is needed to achieve the dissolution of 1-gram uranium in the desired timeframe.

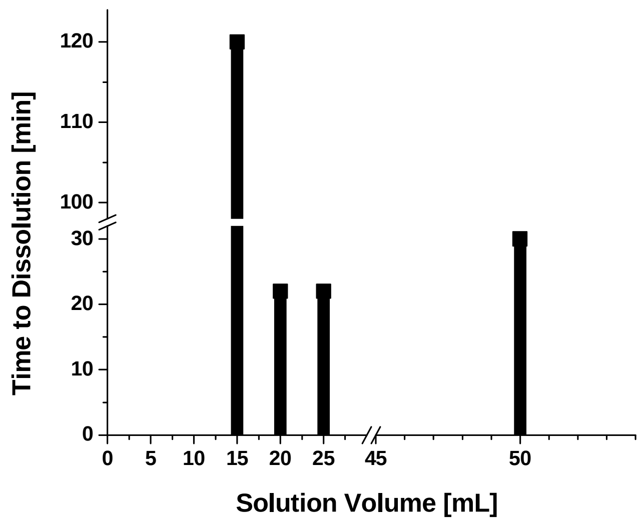

Figure 9: Time to complete dissolution of 1-gram 0.2 mm thick DU turning as function of reagent volume (7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 acid solution).

In any heterogeneous reaction, the interaction between the participating phases strongly influences the rate of reaction. Varying the thickness of the turnings employed in the dissolution process, while keeping all other reaction parameter constant, revealed a direct proportional relationship between dissolution time and turning thickness (see Figure 10). The dissolution time appears to have an inverse quadratic relation to the geometric surface of the bulk material. BET surface area measurements performed on the DU turnings to determine their active surface were discontinued after initial results indicated that the geometric surface area was equivalent to the active surface area. We observed that the dissolution time per gram uranium was not proportional to the surface area. This suggests that the uranium metal dissolution reaction is not controlled by diffusion processes but rather by the chemical processes involved. This is typical for metal dissolutions in oxygen containing acids. Such dissolutions are often characterized by consecutive reaction such as oxidation of the metal to a cation followed by complexation reactions.

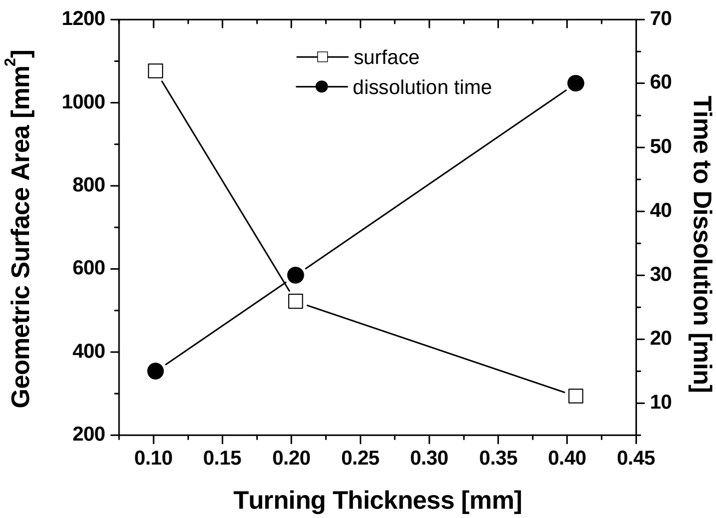

Figure 10. Time to complete dissolution of 1-gram DU turning in 50 mL of 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 acid solution as function of the turning thickness. The geometric bulk surface area for 1-gram DU turning as function of thickness is in inverse quadratic relation to the observed dissolution time.

<u>Reaction Kinetic Study</u>

For the dissolution of DU turnings in 7.5 mol/L sulfuric – 1mol/L nitric acid solution detailed experiments were performed to determine the reaction order, n, and Arrhenius parameter, E_A, the pre-exponential factor, A, the activation enthalpy, $\Delta H^{\neq}$, and the activation entropy, $\Delta S^{\neq}$. Most experiments (see Table 11) were run in duplicate. To determine the reaction order, 4 different initial amounts (0.25, 0.5, 1 and 2 g) of DU turning (0.1 mm) were subjected to 50 mL of the 7.5 mol/L sulfuric – 1mol/L nitric acid mixture at ambient temperature. The Arrhenius and activation parameter were determined by studying the dissolution of 1-gram DU turning (0.1 mm) in 50 mL of the acid mixture at increasing initial reaction temperatures (25, 37, 42, 63, 67, and 70°C).

The uranium concentration as function of time was determined by monitoring the UV/VIS absorbance of the UO_2^{2+} ion at 421 nm. Small aliquots (0.5 mL) were temporarily removed from the reaction vessel to determine the dissolved uranium. Figure 11 illustrates an example for the time dependent UV/VIS spectra obtained, from which the raw data have been taken. The absorbance units, determined at the time of the complete DU metal dissolution, are equal to the amount of uranium subjected to the dissolution reaction; e.g. 20 mg/mL when 1 gram is dissolved in 50 mL. The dissolved uranium concentration at any time during the reaction can then be deduced form the absorbance values measured prior to complete dissolution using the above relation. Before each time series measurement, a dark spectrum and a reference spectrum was taken. Freshly prepared reagent solution was used as reference solution. To monitor the performance of the instrument, uranium standard solutions (2, 4, 8, 12, and 20 mg/mL) in nitric acid were measured in regular intervals.

Table 11: Experimental parameter and dissolution times for the experiments performed to determine the kinetic reaction parameter of the dissolution of metallic DU turnings (0.1-mm) in 50-mL 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 acid solution.

ID	**Experiment to Determine Reaction Order at 25°C**		**Experiments to Determine Arrhenius Reaction Parameter 1-g metal**	
	mass [g]	**Time to Dissolution (min)**	**temperatu re [°C]**	**Time to Dissolution (min)**
2-01	1	14	25	14
2-02	1	20	25	20
2-1			70	3.5
2-2			67	4.5
2-3			42	9
2-4			37	9.25
2-5	0.5	25		
2-6	0.5	17.5		
2-7			63	5
2-8	2	10		
2-9	2	10		
2-10	0.25	20		
2-11	0.25	20		
2-12	0.5	19		

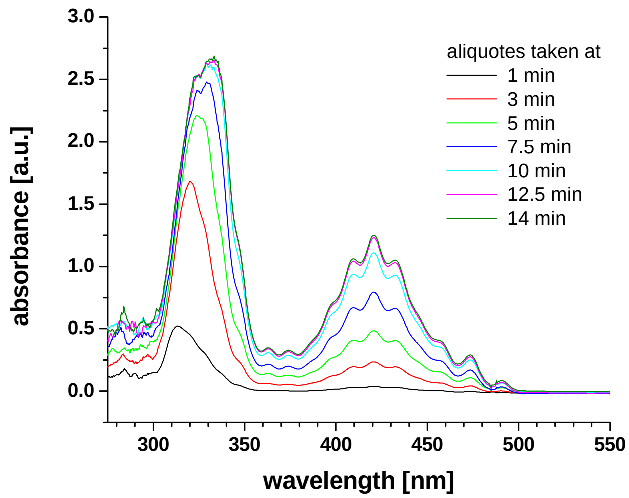

Figure 11. Uranyl ion UV/VIS spectra as function of time during the dissolution of 1 gram DU turning (0.1 mm) in 7.5 mol/L sulfuric – 1 mol/L nitric acid solution.

<u>Kinetic Study Results and Discussion</u>

During the first experiments within the randomized half fractional factorial method series, the uranium concentration was monitored as a function of time. The variation of four parameters (temperature, two individual acid concentration, and turning thickness) at once makes drawing meaningful conclusions from those data exceedingly difficult (Figure 11). The kinetics of the metallic uranium dissolution appears to change significantly with changes in the experimental conditions. An increase in temperature, for instant, resulted in general in an overall accelerated dissolution rate for all systems expect system #1-5.

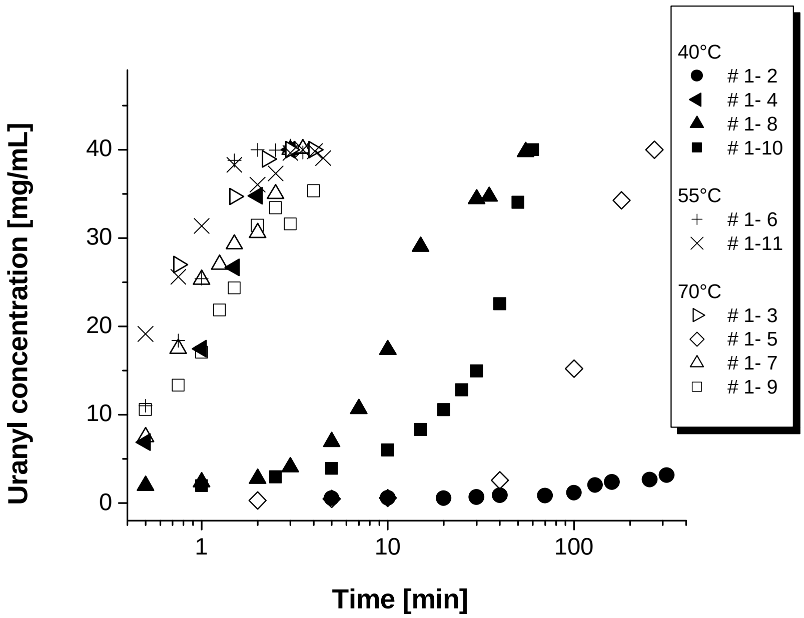

Figure 11. Uranyl ion concentration as function of time for the dissolution of 2-gram DU turnings in 50-mL acid mixtures with varying concentration in HNO_3 (8, 11.5, and 14 mol/L) and in H_2SO_4 (0.1, 1.1, and 2 mol/L), varying metal turning thickness (0.1 and 0.2 mm) as well as increasing initial reaction temperature (40, 55, and 70°C).

The parameters of the reaction kinetic for the dissolution of metallic uranium in 50 mL of 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 acid solution were determined by varying the mass of uranium dissolved and the initial dissolution temperature. The uranium concentration as function of time was monitored by measuring the dissolved uranium in the solution using an UV/VIS spectrometer. Figures 12 and 13 include the data sets used to determine the reaction order and the Arrhenius reaction parameter.

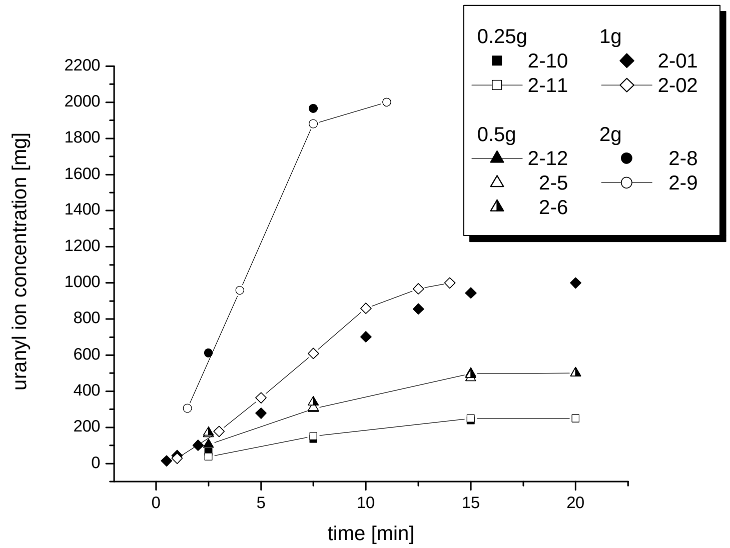

Figure 12: Uranyl ion concentration as function of time for increasing initial DU metal mass (0.1-mm thick turnings) dissolved in 50-mL of 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 acid solution at ambient temperature.

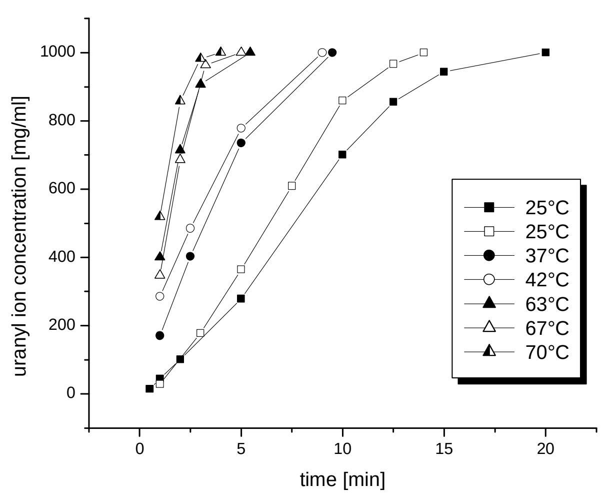

Figure 13: Uranyl ion concentration as function of time for increasing initial reaction temperatures for the dissolution of 1-gram DU turning (0.1-mm thick) in 50-mL of 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 acid solution.

The reaction order was determined using non-integrated rate laws. This method is particularly useful for reaction of higher order and for reaction with complex elementary step that often have fractional orders. Often, the required reaction rates can be determined graphically by constructing tangents on the curves of the concentration-time pairs. A good approximation, the reaction rate can be calculated from the quotient of the difference rather than the differential quotients. This assumption (equation 11) can be made if less than 5% of the initial reactant is consumed within a given reaction interval.

$$r \cong \Delta[U] / (\nu_U * \Delta t) \qquad (11)$$

Based on the log arithmetic rate law for reactions of higher order:

$$\lg r = \lg k + n \lg [U] \qquad (12)$$

the reaction order can then be deduced if two concentration – rate couples are known:

$$n = \lg (r'/r'') \ / \ \lg ([U]'/[U]'') \qquad (13)$$

This method is primarily applied to the immediate start of a reaction, but can be used for other conditions as well. For a reaction of n-th order, n can be determined using equation (13), where [U]' and [U]" represent two different initial concentrations of uranium.

A more accurate method of determining reaction rate is to create a graph of lg r as function of lg [U]. The slope of this function provides directly the reaction order (see equation 12). The data given in Table 12 were calculated from the concentration vs. time plots shown in Figure 12 and were used to create the graph of lg [r] as function of lg [U] shown in Figure 14. From the linear regression fit of Figure 14 the following rate law (equation 14) can be established for the dissolution of metallic uranium in 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3:

$$r = 1/\nu_U \, d[U]/dt = k \, [U]^{2.5} \quad (14)$$

This fractional order for the metallic uranium dissolution compares well to the hypothesized complex elementary reactions occurring, which include chemical and physical processes.

Table 12. Data, deduced from concentration-time function applied to determine the reaction order of the metallic uranium dissolution in 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 at ambient temperature.

Initial DU mass $[U_0]$ **in g**	**Remaining DU at Δt [U] in g**	**Time Interval Δt in s**	**Reaction Rate r in mol L^{-1} s^{-1}**
2	1.9	123	0.001298
1	0.95	75	0.001064
0.5	0.475	53	0.000753
0.25	0.2375	34	0.000587

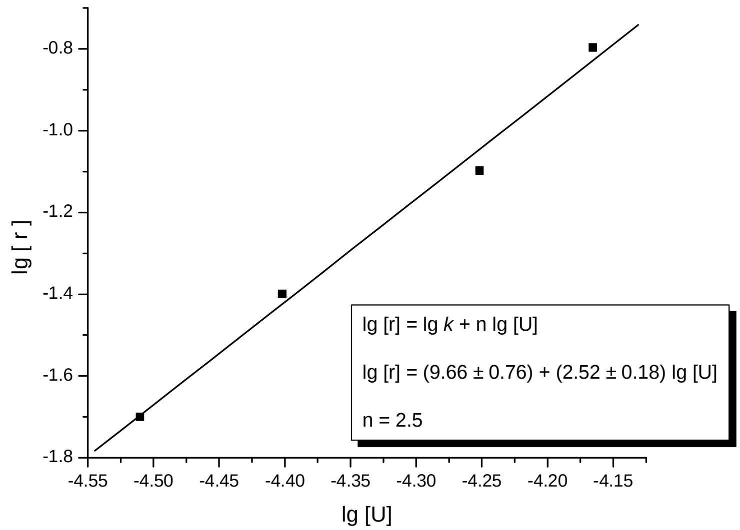

Figure 14: Graphic determination of reaction order for the metallic uranium dissolution utilizing the experimentally determined data and graphing lg [r] as function of lg [U].

The activation energy of a reaction can be determined by using the Arrhenius Law (equation 15):

$$\ln k = \ln A - E_A/RT \qquad (15)$$

Experiments, performed at different initial temperature, provide the concentration vs time functions needed to deduce the data for ln k as function of 1/T. Figure 15 illustrates the concentration vs time function we obtained for six different initial temperatures. The established rate law was applied to the data shown in Figure 15 in order to determine the temperature dependent reaction constants for the dissolution reaction of 1-gram DU turnings in 50 mL of 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3. The reaction rates at the different initial temperatures were determined according to equation 11, for the initial period of the reaction. Table 13 summarizes the kinetic reaction data calculated from the experimental results.

Table 13. Elapsed reaction time for the dissolution of initial 50 mg of 1 g DU in 50 mL at increasing temperature and reaction parameters deduce on the basis of the established rate law (equation 14).

Temperature °C	Δt s	Reaction rate, r mol $L^{-1.5}$ s^{-1}	Reaction constant, *k* mol $L^{-1.5}$ s^{-1}	1/T K^{-1}
25	75	5.60E-05	3.11E-02	3.35E-03
37	18.6	2.26E-04	1.25E-01	3.22E-03
42	10.2	4.12E-04	2.29E-01	3.17E-03
63	8.4	5.00E-04	2.78E-01	2.97E-03
67	7.2	5.84E-04	3.24E-01	2.94E-03
70	5.58	7.53E-04	4.18E-01	2.91E-03

The slope of the graph of ln *k* as function of 1/T yields the activation energy according to equation 5 (Figure 15). We determined an activation energy for the dissolution of metallic uranium in 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 of 92.5 ± 20.5 kJ mol^{-1} K^{-1}.

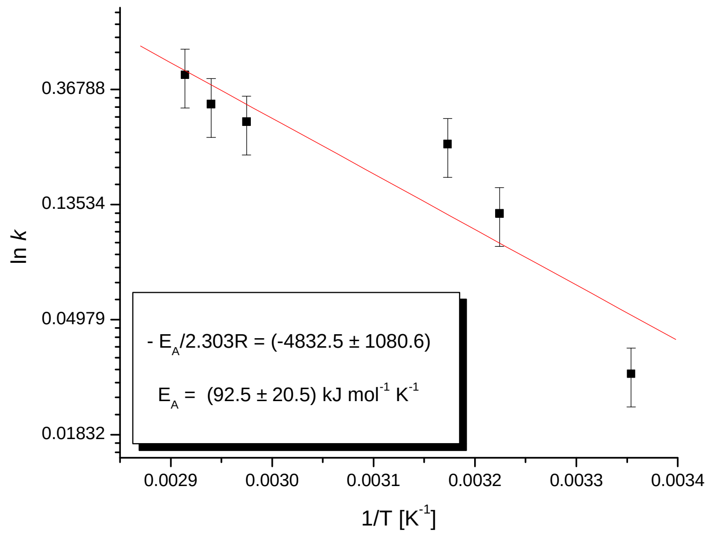

Figure 15. Graphic determination of the activation energy, E_A, for the metallic uranium dissolution in 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 from the experimentally determined data of ln k as function of 1/T.

Determination of the activation energy of a reaction allows the calculation of the activation enthalpy of the reaction (equation 16). The activation entropy, $\Delta S^{\neq}$, (equation 17) can be determined using the pre-exponential parameter, A, of the Arrhenius equation (equation 15), where the pre-exponential parameter, A, is calculated by a linear fit regression of ln k as function of 1/T.

$$E_A = \Delta H^{\neq} + RT \qquad (16)$$

$$\Delta S^{\neq} = 19.15 \lg (A/T) - 205.9 \qquad (17)$$

$\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated for the dissolution reaction of metallic uranium in 7.5 mol/L H_2SO_4, 1 mol/L HNO_3 and were found to equal 90.0 ± 19.8 kJ mol^{-1} K^{-1} and -231.8 ± 58.6 kJ mol^{-1} K^{-1}, respectively.

Reaction Enthalpy Study

A Parr 1455® solution calorimeter was employed to determine the heat evolved during the dissolution of metallic uranium in the 7.5 mol/L sulfuric – 1mol/L nitric acid mixture. The calorimeter had a working temperature range from 0 to 70°C with a temperature sensitivity to 0.0002°C. The optimum energy measurement range is 8 to 4187 J and the detectability limit is 0.4 J. The calorimeter was calibrated for the specific reaction condition by electrical standardization. The calorimeter was filled with 75 mL of 7.5 mol/L sulfuric – 1mol/L nitric acid solution. After the temperature of the solution in the calorimeter had stabilized, a well-defined energy amount (57.5 ± 2.9 J) was supplied to the solution by an electrical heating probe (Parr AC274C). The calibration was repeated six times. The evolving heat in the system was monitored by a temperature sensor submerged in the solution and read and stored by a LabView® routine to a comma delimited computer file. The energy equivalent for the system prior to adding the uranium was determined to be (332.2 ± 23.3) J K^{-1}.

The experiments to determine the reaction enthalpy of the dissolution of the metallic uranium in the 7.5 mol/L sulfuric – 1mol/L nitric acid mixture consisted of three duplicate measurements. In all experiments 75 mL of the solution was placed in the calorimeters dewar. Once the temperature of the solution stabilized to a constant temperature, the DU turnings were released into the solution. The temperature of the system was recorded in 10-second intervals.

Reaction Enthalpy Study Results and Discussion

Calorimetric measurements of the heat evolved during the dissolution of 1 gram DU turnings (0.1mm) in 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 were completed to better understand reaction thermodynamics. The experimental conditions and results are presented in Table 14. The enthalpy was calculated using the basic caloric equation:

$$Q = c\,\Delta T \tag{18}$$

The energy equivalent, c was determined prior to the to the uranium dissolution studies. ΔT was determined graphically at the point where 63% of the reaction total energy had been released. The reaction clearly generates heat and is exothermic. The reaction enthalpy of the metallic uranium dissolution in 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3 was determined to be approximately -1021 kJ/mol. We chose not to average the reaction enthalpies obtained at three different masses, because only the experiments using 0.75 g DU were within the instruments specifications for allowable heat production. We also observed that as the amount of DU dosed to the calorimeter was increased the heat capacity of the resulting solution at the end of the dissolution deviated substantially from the initial solution. The reaction enthalpy that we determined is of the same value as the formation enthalpy of the uranyl ion, which seems a plausible observation. The reaction enthalpy calculated indicates that the contributions to the overall reaction enthalpy from any complexation step is minor compared to the enthalpy contributions from the oxidation reactions involved in the formation of the uranyl ion.

Table 14. Calorimetric experiments and results obtained, given masses of DU turnings (0.1 mm) were reacted in Parr 1455® solution calorimeter with 75 mL of 7.5 mol/L H_2SO_4 – 1 mol/L HNO_3.

DU mass g	DU mol	Temp. at 63% Q °C	ΔT at 63% Q K	Heat, Q, J	**Enthalpy, ΔH** **kJ/mol**	Ø enthalpy, ΔH, at Temperature of 63% Q kJ/mol	Ø Temp. of 63% Q °C
0.75	0.00315	32.79	9.6	3189.05	1012.4	1021.4 ± 71.5	32.4
0.75	0.00315	32.01	9.77	3245.52	1030.32		
1.5	0.0063	36.97	18.73	6221.96	987.613	1000.8 ± 70.1	37.8
1.5	0.0063	38.61	19.23	6388.06	1013.98		
3	0.0126	49.73	36.95	12274.5	974.17	975.4 ± 68.3	49.2
3	0.0126	48.76	37.04	12304.4	976.54		

Proposed Reaction Mechanism

All our experiments were designed to provide insight into the possible reaction mechanism of the metallic uranium dissolution. In addition to the reaction order and thermodynamic data we previously determined, several qualitative observations influenced the elucidation of a plausible reaction mechanism.

We observed a yellowish green solution at the conclusion of the dissolution reaction which suggests that the reaction produces the +4 oxidation state of the uranium. The characteristic colors for the U^{4+} and UO_2^{2+} are green and yellow, respectively. Since either U^{4+}

or UO_2^{2+} could contribute to the color observed, we wanted to determine if the dissolution reaction described in equation 9 could be part of the reaction mechanism.

$$U + 4\,H^{+} \rightarrow U^{4+} + 2\,H_2 \qquad (19)$$

If reaction 9 were occurring, it would be followed by the oxidation of U^{4+} to UO_2^{2+} by the nitric acid or the oxygen contained in the solution. Reaction 9 would produce two moles of colorless hydrogen gas for every mole of uranium dissolved. We measured only to 0.6 moles of brown colored gas being generated per one gram of uranium dissolved. The brown color of the gas indicates the formation of a nitrous gases, suggesting that the nitric acid accomplishes the oxidation of the uranium not the reaction 9. In Equation 10 a possible reaction mechanism is given for the dissolution of uranium in 7.5 M H_2SO_4/1 M HNO_3. This reaction closely predicts the amount of gas generation we observed and includes the immediate oxidation to the +4 oxidation state of the uranium. We recognize that the reaction proposed in 10 is an overall reaction. In order to determine the elementary reaction occurring during the dissolution of metallic uranium, more in depth investigations that were outside of our project's scope would be required.

$$8\,U + 32\,HNO_3 \rightarrow 8\,U^{4+} + 24\,NO_3^{-} + NO + 3\,NO_2 + N_2O + N_2 + 16\,H_2O \qquad (20)$$

PRE-TREATMENT STUDY

Waste DU varies significantly from the well- characterized DU turning used in previously described studies. Differences include the composition, size, age and degree of corrosion of the DU and the fact that the DU is immersed in a variety of solutions to minimize contact with during storage. Grab samples of DU were collected from 6 different waste containers for use in the pre-treatment studies. Four samples of turnings were collected: turnings stored in 2 different coolant solution, water, and mineral oil. Sludge samples stored in mineral oil and 1 coolant solution were also collected. A total of 2 kg of DU waste was collected. The composition of the waste DU samples varied considerably. Our initial efforts with the DU samples focused on characterization using analytical instruments that are readily available to the HWM waste treatment group. Both the DU and the storage solutions were analyzed using an X-ray diffraction, XRF, a GC-MS, a TOC analyzer, and a scintillation counter. The XRF is undergoing additional calibration to improve the quality of the data.

Most of the DU storage solutions have a high concentration of organic compounds which are incompatible with the acids selected for dissolution. Therefore, pretreatment is required to remove all traces of storage solution from the DU solids. An additional goal of pretreatment is to obtain a defined and reproducible starting condition for the subsequent acid dissolution treatment process. A pretreatment study was designed to determine the most effective pretreatment process. The independent variables were wash solution type, concentration and volume; number of wash/rinse cycles; and method of agitation. We used a factorial screening design treating all six variables as noncontinuous, to reduce the number of experiments. There were four different wash solutions, three types of turnings, and two settings each for the other four variables. The wash solutions evaluated included 1) tap water, 2) mild acid (0.1 M HNO_3), 3) TrimTask2, a commercial coolant wash solution, and 4) Ensolv, a commercially available metal washing solvent typically used with vapor degreasing systems. Agitation was provided by either an orbital shaker or an ultrasonic bath. The dependent factor in the pretreatment study was the percentage of TOC removed from the turnings.

The results of the pretreatment study are summarized in Table 16. The type of storage solution and the age of the turnings both influenced the treatment efficiencies observed in the pretreatment study. Turnings stored in mineral oil achieved higher cleaning efficiencies than turnings stored in TrimSol, an organic based coolant solution. Our desire was to select a washing regime that would be applicable to all of the turnings, independent of the type of turning or storage solution. The most effective washing for the various DU turnings was accomplished using a concentrated, surfactant based wash solution, an ultrasonic bath and a total of 2 wash/rinse cycles.

Table 15. Characteristics of depleted uranium waste used in pretreatment study.

Sample ID	Description	U metal composition	Storage solution TOC	Storage solution gross alpha and gross beta activity (mCi/mL)
R000569	Large turnings and sediment in clear liquid	U, Pb	1390 mg/l	1.65e-9 α 5.33e-9 β
W111280	Turnings in bluish-white coolant	U, Nb	5500 mg/L	7.8e-8 α 1.0e-7 β
W111325	Turnings in yellow coolant	U, Nb, Zr	1900 mg/L	2.8 e-8 α 6.6 e-8 β
W105528	Black sludge with clear liquid (mineral oil)	U, Nb, Zr		1.9 e-8 α 1.1 e-8 β
W111257	Coarse sludge with greenish-blue coolant	U, Nb	6200 mg/l	3.2 e-7 α 1.4 e-6 β

Table 16. Pretreatment study results.

Turnings source	Cleaning solution	Solution conc	Solution volume	Ultrasonic or shaker	Repeat cycle	Initial TOC	Final TOC	% Remove
Coolant 2 W111357	Water	N/a	100 ml	Ultrasonic	Yes	69.4	13	81.3
Mineral oil	Water	N/a	200 ml	Shaker	No	65.5	31	52.7
Coolant 2 W111357	Acid	0.1M	200 ml	Shaker	Yes	69.4	38.8	44
Mineral oil	Trimtask	1:1	100 ml	Shaker	No	65.5	50.5	22.5
Mineral oil	Acid	0.5M	100 ml	Ultrasonic	No	65.5	65	0
Mineral oil	Acid	0.1M	100 ml	Ultrasonic	Yes	65.5	17.6	54
Coolant 1 W111280	Water	N/a	100 ml	Ultrasonic	No	119.8	80	33
Coolant 1 W111280	Trimtask	1:1	200 ml	Ultrasonic	Yes	119.8	39	67.4
Mineral oil	Trimtask	1:10	200 ml	Ultrasonic	Yes	65.5	52	20.58
Coolant 2 W111357	Trimtask	1:10	100 ml	Shaker	No	69.4	25	64
Coolant 1 W111280	Acid	0.5M	200 ml	Shaker	No	119.8	87	27
Coolant 1 W111280	Water	N/A	100	Shaker	Yes	119.8	66	45
Mineral oil	Water	N/A	200	Shaker	Yes	65.5	69.5	0
Coolant 2 W111357	Water	N/A	200	Ultrasonic	No	69.4	29.8	57
Coolant 2 W111357	Acid	0.1M	200 ml	Shaker	Yes	69.4	45.5	34
Coolant 1 W111280	Trimtask	1:1	200 ml	Ultrasonic	Yes	119.8	59.8	50
Mineral oil	Trimtask	1:10	200 ml	Ultrasonic	Yes	65.5	34.5	47.3
Mineral oil	Water	N/A	200	Shaker	Yes	65.5	64.3	0

SUMMARY AND CONCLUSIONS

Our investigations determined that an acid solution of 7.5 mol/L in sulfuric and 1 mol/L nitric acid, is a viable acid mixtures for the dissolution of metallic uranium at ambient temperature. One gram of uranium metal turnings is dissolved in 50 mL of this solution in 12 to 60 minutes, depending on the thickness of the turning. The optimum solid to liquid ratio appears to be 1gram uranium to 20 mL acid solution. Increasing the acid volume beyond this level does not improve the dissolution process, but rather contributes to an increase in secondary waste requiring disposal.

The dissolution time per gram uranium appears not to be proportional to the surface area, which indicates that the uranium metal dissolution reaction is controlled by the chemical elementary reactions involved rather than by any of the physical processes that often dominate heterogeneous reaction, such as diffusion, sorption and desorption processes. This observation is typically made for metal dissolutions in oxygen containing acids. Such dissolutions are generally characterized by consecutive reaction, e.g., oxidation of the metal to a cation followed by complexation mediated dissolution.

Our kinetic investigations revealed for the first time that the uranium metal dissolution in the solution of 7.5 mol/L sulfuric and 1 mol/L nitric acid is of the fractional order of 2.5. This result and that the rate law could not be limited to a pseudo first order, the usual case for a reaction where one component is supplied in excess, nor to a zero order reaction, typical for complex reaction and reaction dominated by physical processes at an interface, documents to complexity of the chemical elementary reaction involved in the dissolution of metallic uranium in oxygen-containing acids used. The activation energy, activation enthalpy and activation entropy were experimentally determined to be (92.5 ± 20.5) kJ mol^{-1} K^{-1}, (90.0 ± 19.8) kJ mol^{-1} K^{-1} and (-231.8 ± 58.6) kJ mol^{-1} K^{-1}, respectively. The calorimetrically determined reaction enthalpy of 1021 kJ/mol further substantiate the dominance of the oxidation processes in the dissolution of metallic uranium, as the enthalpy determined equals the formation enthalpy of the uranyl ion. Although a reaction mechanism for the initial fast oxidation of the metal uranium to U^{4+}, which is followed by oxidation to the uranyl ion, is hypothesized in equation 20, elementary reaction processes could not be deduced from the experimental data we obtained. The here established kinetic and thermodynamic data, however, will be potentially essential for the design of a large-scale metallic uranium waste treatment process.

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REFERENCES

Cordfunke, E.H.P., O'Hare, P.A.G., The Chemical Thermodynamic of Actinide Elements and Compounds, Part 3, IAEA, 1978.

Fuger, J., Kjodakovsky, I.L., Sergeyeva, E.I., Medvedev, V.A., Navratil, J.D. 1992. The Chemical Thermodynamic of Actinide Elements and Compounds, Part 12, IAEA.

Czupryna, G., Levy, R.D. and Gold, H. 1987. "Selective Dissolution and Recovery of Depleted Uranium From Amor Plate. Foster-Miller, Inc. Final Report #MER-0017-FMI-8644-80.

D. Dong, G. F. Vandegrift. 1996. *Nucl. Science & Eng.* **124,** 473-481.

Hightower, J.R., and Trabalka, J.R. 2000. Depleted Uranium Storage and Disposal Trade Study: Summary Report. Oak Ridge National Laboratory Report #ORNL/TM-2000/10.

Katz, J.J. and Rabinowitch, E. 1951. Chemistry of Uranium. McGraw-Hill Book Co., New York, New York.

Katz, J.J., Seaborg, G.T., Morss, L.R.. 1986. The Chemistry of the Actinide Elements, Vol. 1, 2nd edition, Chapman and Hall, London, pp. 169

Larsen, R.P. 1959. "Dissolution of Uranium Metal and Its Alloys." Analytical Chemistry. Vol. 31, p 545-549.

Lussiez, G. and Zygmunt, S. 1993. The Hazardous Waste Treatment Facility and Skid-mounted Treatment System at Los Alamos. LANL report # LA-UR-93-1205.

N. N. Sauer, J. G. Watkin. 1992. U.S. Patent 5098677.

Roden, C.J. 1950. Analytical Chemistry of the Manhattan Project. McGraw-Hill Book Co., New York, New York.

Rodrigues L.S., Falleiros, N.A., deO.Forbicini, C.A.L.G., J. 2002. Radioanal. Nucl. Chem 253, 511-515.

Wanner, H., Forest, I., Eds. 1992. Chemical Thermodynamics of Uranium, North-Holland, Amsterdam.